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EFFECT OF CHROMIUM-CONTAINING ADDITIVES ON THE STRUCTURE OF SPINEL-TYPE PIGMENTS

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Self-propagating high-temperature synthesis was used to synthesize rose-colored corundum and spinels with chromium-containing additives. The synthesized pigments can be used to decorate porcelains and other ceramic articles.

Self-propagating high-temperature synthesis (SHS) has been used to synthesize cobalt-containing spinel-type pigments. The SHS method, based on the use of the heat generated by exothermal reactions, has made it possible to obtain pigments which have a high resistance to heat, moisture, and chemicals. The introduction of chromium-containing additives has a large effect not on only the color of the pigments obtained but also on their structure.

The aim of the present work is to obtain spinel-type ceramic pigments by SHS and to study the effect of chromium-containing additives on their color, composition, and structure.

The compounds Al_2O_3, Co_2O_3, Co_3O_4, Cr_2O_3, CrO_3, ZnO, and MgO and ASD-4 aluminum powder were used to synthesize the pigments. The synthesis was done in a constant-pressure apparatus.

The pigments obtained were identified by x-ray phase analysis performed with a DRON-UM1 diffractometer (filtered CoK_α radiation) and by infrared spectroscopy in the range 4000 – 400 cm^{-1} using the Nicolet-5700 IR-Fourier spectrometer on the attachment for diffuse reflection in KBr.[2] The microstructure of the samples was investigated using light microscopy (Axiovert 200M, Unimet) and scanning electron microscopy (Camebax), which was also used for x-ray microprobe spectral analysis.

Chromium compounds are widely used as chromophores in the synthesis of ceramic pigments. It is known that the degree of oxidation of chromium can range from 0 to 6+. If the degree of oxidation of chromium is 3+, then the coordination number of Cr^{3+} is 6 and the structure of the complexes is octahedral; the coordination number 4 and tetrahedral structure are characteristic for Cr^{6+}. Depending on the degree of oxidation and the coordination number of the complex-forming ion, the color due to the oxygen compounds of chromium can vary from green to rose [1].

A rose-colored pigment was synthesized by the SHS method using aluminum and chromium oxides (Al_2O_3, CrO_3, or Cr_2O_3). X-ray phase analysis showed that the compound obtained is corundum. IR spectroscopy also confirms this (Fig. 1). The Al^{3+} ions in the crystal lattice of corundum (Al_2O_3) are replaced with Cr^{3+} ions, and the length of the chemical bond between Cr^{3+} and O^{2-} is observed to decrease, which increases the energy splitting due to the field of the ligands and converts the green color to red. Rose chromium pigments in the series $Al_2O_3 – Cr_2O_3$ are colored corundum compounds which the character of the light absorption curves shows to be similar to natural ruby.

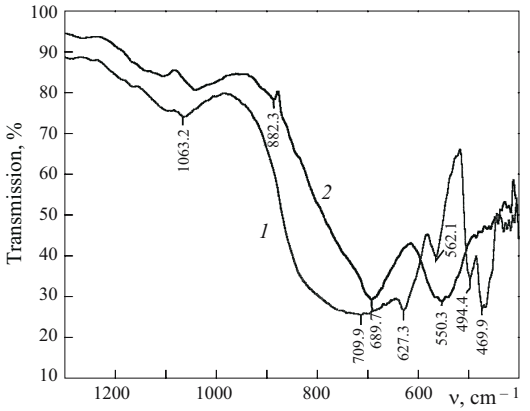

Fig. 1. IR spectra of the pigments: *1*) rose corundum; *2*) rose spinel.

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[2] The IR-spectroscopic studies were performed using the equipment at the Scientific-analytical Center at Tomsk Polytechnic University.

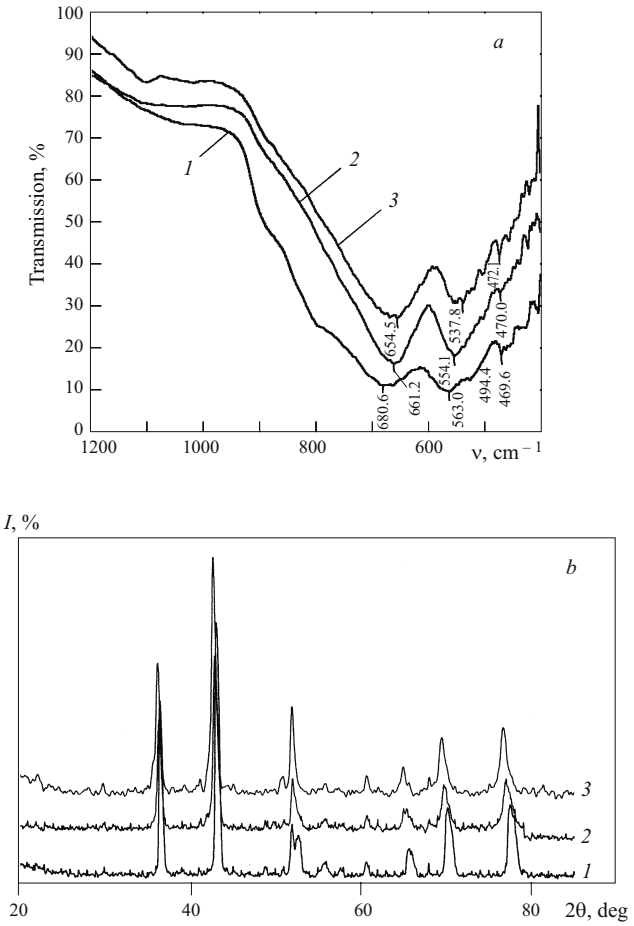

Fig. 2. IR spectra (*a*) and x-ray diffraction patterns (*b*) of pigments in the system ZnO – CoO – Cr_2O_3 – Al_2O_3: *1*) UKTsKh; *2*) UKTsKh-1; *3*) UKTsKh-2.

Synthesis in the system MgO – Al_2O_3 with additions of CrO_3 also results in a rose-colored pigment. IR spectroscopy and XPA show that a spinel-type pigment forms. The color of the pigment is due to the tetrahedrally coordinated Cr^{6+} ion in spinel. Absorption bands at 550.3 cm^{-1} due to octahedrally coordinated aluminum and 689.7 cm^{-1} due to tetrahedrally coordinated magnesium and chromium ions are observed in the IR spectrum.

Synthesis in the system ZnO – CoO – Cr_2O_3 – Al_2O_3 with different Cr_2O_3 content gives blue-green pigments. The degree of oxidation of chromium in Cr_2O_3 is 3+, and the structure of the chromium ion in spinel is octahedral. The classic IR spectrum of the spinel structure, characterized by absorption bands at 563.0, 554.1, and 537.8 cm^{-1} due to aluminum ions occupying octahedral voids and 680.6, 661.2, and 654.5 cm^{-1} due to Co ions in tetrahedral voids is observed (Fig. 2*a*). The vibrations of the zinc-ion bonds are manifested at 469.6, 470.0, and 472.1 cm^{-1}. In the present case, the vibrations of the octahedrally coordinated chromium ions coincide with the vibrations of the aluminum-ion bonds [2, 3]. Synthesis gives solid solutions between aluminum-cobalt spinel and chromium-spinel of cobalt. The substitution of the heavier chromium atom for the lighter aluminum ion (with an increase of the Cr_2O_3 content) shifts the absorption bands in the IR spectrum into the low-frequency range, which attests to the appearance of solid solutions.

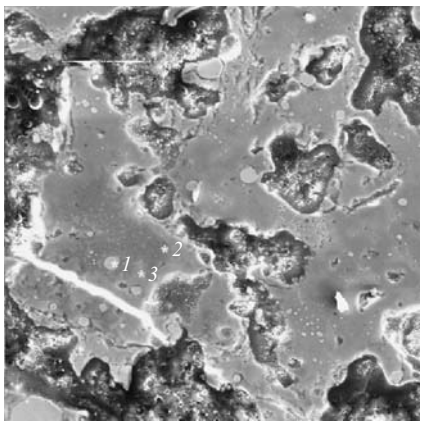

Fig. 3. Microstructure of pigment in the system ZnO – CoO – Cr_2O_3 – Al_2O_3 (× 400): *1*) Co; *2*) $CoAl_{2-x}Cr_xO_4$; *3*) $CoAl_{2-y}Cr_yO_4$ ($y > x$).

The formation of solid solutions is also confirmed by the shift of the diffraction maxima in the direction of smaller angles (Fig. 2*b*). The parameter *a* of the unit cell in the cubic system of the crystal lattice of spinels in system ZnO – CoO – Cr_2O_3 – Al_2O_3 also increases with increasing concentration of Cr^{3+}, which replaces Al^{3+}, and equals 8.1075 Å (the pigment UKTsKh), 8.1134 Å (UKTsKh-1), and 8.1593 Å (UKTsKh-2) [4].

The microstructure of the pigment in the system ZnO – CoO – Cr_2O_3 – Al_2O_3 is shown in Fig. 3. Regions *2* and *3* of aluminum-chromium-cobalt spinel less and more, respectively, enriched with chromium are observed together with inclusions *1* of metallic cobalt.

The color of the chromium-containing pigments depends on the structure of the compound obtained, the degree of oxidation, and the coordination number of the chromium ion present in spinel. When Cr^{3+} ions replace Al^{3+} ions in corundum, the pigment becomes rose colored. Spinels in which the Cr^{6+} ion occupies tetrahedral voids are rose-colored. Octahedrally coordinated Cr^{3+} ions impart a blue-green color to blue spinels.

The pigments synthesized can be used for decorating porcelains and other ceramic articles.

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